# CONCISE ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

Jacqueline I. Kroschwitz, *Executive Editor*

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### Software

Software packages are available for dealing with polymers, but mainly biopolymers; these include SYBYL (Tripos Associates), INSIGHT (Biosym Technologies), QUANTA (Polygen Corp.), CHEMX (Chemical Design Ltd.), and others. The software produces representations of ribbon structures, space-filling structures, molecular surfaces, and molecular orbital diagrams.

### Techniques

Molecular graphics is used extensively as a tool in biotechnology.

**Biopolymers.** The various advances of graphics in biopolymers (proteins and peptides, nucleic acids, and sugars) led to a complete description of 3-d structural analysis of macromolecules.

**Catalysts and Inorganic Polymers.** Modeling has been used for zeolites, which are crystalline aluminosilicates whose 3-d framework consists of corner-sharing SiO and AlO tetrahedrons.

**Synthetic Polymers.** The prediction of properties of synthetic polymers computationally has been developed since the late 1960s. As the cost of industrial research has risen and as polymers have moved increasingly into more specialized high performance areas, interest in molecular graphics applications to synthetic polymers has increased dramatically.

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ROY J. VAZ
Tripos Associates

NEELA SRINIVASAN
University of North Carolina


## MOLECULAR WEIGHT AVERAGE.

See MOLECULAR WEIGHT DETERMINATION.

## MOLECULAR WEIGHT DETERMINATION

### Molecular Weight Averages and Distributions

Most polymeric materials are composed of mixtures of molecules of various sizes. This distribution of molecular weights is caused by the statistical nature of the polymerization process. A complete description of the molecular weight distribution of a polymer is necessary to understand its physical, rheological, and mechanical properties.

Certain techniques for molecular weight determination are only capable of yielding one of the molecular weight averages of the distribution. These averages are defined in terms of the molecular weight $M_i$ and the number of moles $n_i$ or the weight $w_i$ of the component molecules. The molecular weight averages are defined by equations 1–5.

*Number-average molecular weight:*

$$\bar{M}_n = \frac{\Sigma n_i M_i}{\Sigma n_i} = \frac{\Sigma w_i}{\Sigma w_i / M_i} \tag{1}$$

*Weight-average molecular weight:*

$$\bar{M}_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} = \frac{\Sigma w_i M_i}{\Sigma w_i} \tag{2}$$

*z-Average molecular weight:*

$$\bar{M}_z = \frac{\Sigma n_i M_i^3}{\Sigma n_i M_i^2} = \frac{\Sigma w_i M_i^2}{\Sigma w_i M_i} \tag{3}$$

*(z + 1)-Average molecular weight:*

$$\bar{M}_{z+1} = \frac{\Sigma n_i M_i^4}{\Sigma n_i M_i^3} = \frac{\Sigma w_i M_i^3}{\Sigma w_i M_i^2} \tag{4}$$

*Viscosity-average molecular weight:*

$$\bar{M}_v = \left[\frac{\Sigma n_i M_i^{1+\alpha}}{\Sigma n_i M_i}\right]^{1/\alpha} = \left[\frac{\Sigma w_i M_i^{\alpha}}{\Sigma w_i}\right]^{1/\alpha} \tag{5}$$

### Molecular Weight Distribution Functions

Various mathematical functions have been employed to describe the distribution of molecular weights. Some of the more common functions are shown in Table 1 in terms of the mole fraction $X$.

### Determination of Molecular Weight

**Number-average Molecular Weight.** Number-average molecular weight can be determined by end group analysis and measurement of colligative properties (ebulliometry, cryoscopy, membrane osmometry).

**Viscosity-average Molecular Weight.** The viscosity of dilute polymer solutions may be related to the molecular weight of the polymer by the appropriate calibration. The polymer is usually separated into narrow molecular weight distribution fractions, which are characterized by absolute molecular weight methods. The molecular weight is related to the intrinsic viscosity $[\eta]$ by the Mark-Houwink relationship.

**Weight-average Molecular Weight.** Weight-average molecular weight can be determined by light scattering and ultracentrifuge techniques.

**Higher Molecular Weight Averages.** Classic techniques often cannot be used for higher molecular weight averages ($\bar{M}_z$, $\bar{M}_{z+1}$, etc). These are usually measured by determining the molecular weight distribution by fractionation or chromatography and back-calculating the averages from the distribution.

### Determination of Molecular Weight Distribution

Methods used to determine the molecular weight distribution include fractionation (qv); various forms of chromatography (qv), including gel-permeation or size-exclusion, thin layer, high performance liquid chromatography, supercritical fluid

Table 1. Molecular Weight Distribution Functions

| Name | Function | Comments |
|---|---|---|
| Gaussian | $X(M) = \frac{1}{\sigma_n(2\pi)^{1/2}} \exp\left[\frac{(M - M_m)^2}{2\sigma_n^2}\right]$ | $M_m$ = median value equal to $\overline{M}_n$ |
| log-normal | $X(M) = \frac{1}{\sigma_n(2\pi)^{1/2}} \exp\left[\frac{(\ln M - \ln M_m)^2}{2\sigma_n^2}\right]$ | $M_m$ = geometric mean |
| Poisson[a] | $X(M) = \frac{\nu^{M-1}}{\Gamma(M)} \exp(-\nu)$ | $\nu = \overline{M}_n - 1$ |
| Flory-Schulz[b] | $X(M) = \frac{\beta^{k+1}M^{k-1}\overline{M}_n}{\Gamma(k+1)} \exp(-\beta M)$ | $k$ = degree of coupling $\beta = \frac{k}{\overline{M}_n}$ |

[a] $\Gamma(M) = \gamma$-function.
[b] $\Gamma(k + 1) = \gamma$-function.

chromatography, phase-distribution chromatography, field-flow fractionation; electrophoresis (qv); and atomization of polymer solutions.

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ANTHONY R. COOPER
Lockheed Missiles & Space Company, Inc.

## MOLECULAR WEIGHT DISTRIBUTION. See FRACTIONATION.

## MONODISPERSE POLYMERS

The preparation of homopolymers and block copolymers with near monodisperse (uniform) molecular-weight distributions is of both academic and commercial value. The absence, in certain cases, of a spontaneous termination step during propagation allows for the preparation of linear and star-shaped polymers. This facilitates studies in block polymer morphology, chain dynamics, diffusion (both tracer and self-diffusion), unperturbed chain dimensions, and rheology. These investigations have benefited from the narrow distribution of chain lengths present in the samples. The materials evaluated have been prepared by anionic polymerization of dienes and by hydrogenation of these polydienes.

In any consideration of molecular weight distributions resulting from termination-free systems, the potential influence of the relative rates of initiation and propagation must be recognized. Quantitative relations have been developed between the molecular weight distribution and the ratio of propagation to initiation rates. Even in the extreme case where $k_p/k_i = 10^6$, the resultant $x_w/x_n$ ratio does not exceed ~1.4. Termination-free polymerizations, in which the active center has two forms in dynamic equilibrium with each exhibiting its own propagation rate have been examined. This approach has been used to develop a method for dissecting $k_p$ into the contributions from the various ionic structures of the propagating center in polar media from an analysis of the resultant molecular weight distributions. Any desired polydispersity in molecular weights is obtained by controlling the addition of initiator during a nonterminating polymerization.

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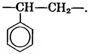
LEWIS J. FETTERS
Exxon Research and Engineering Company

## MONOMER

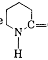
A monomer is defined as a compound consisting of molecules, each of which can provide one or more constitutional units of a polymer (or oligomer). For example, the monomer molecule styrene (—CH=$CH_2$) provides the constituent unit



The monomer molecule $CH_2$=CH—CH=$CH_2$ can provide the constitutional units

$$—CH_2CH{=}CHCH_2— \quad \text{or} \quad \begin{array}{l}—CHCH_2—\\ \quad | \\ \ \ CH{=}CH_2\end{array}$$

The monomer molecule $CH_2N_2$ can provide the constitutional unit —$CH_2$—.

A monomer molecule of δ-valerolactone  can pro-